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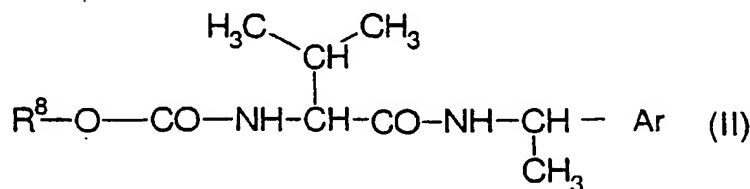
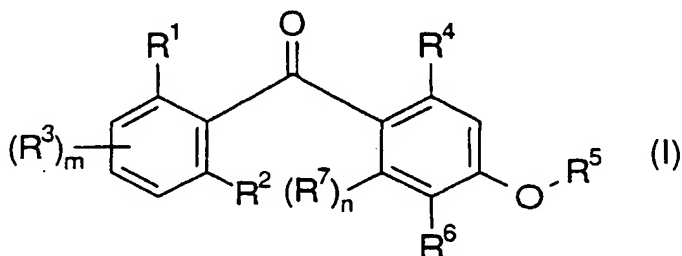
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(54) Title: FUNGICIDAL MIXTURES



(57) Abstract: The invention relates to a novel fungicidal composition comprising a fungicidally acceptable carrier and/or surface active agent and synergistically effective amounts of (a) at least one benzophenone of formula (I) wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, m and n have the meaning given; at least one compound of formula (II) in which Ar and R<sup>8</sup> have the meaning given; and to a method of controlling the growth of phytopathogenic fungi at a locus which comprises applying synergistically effective amounts of (a) at least one benzophenone of formula (I) and (b) at least one compound of formula (II) to the locus.

## Fungicidal mixtures

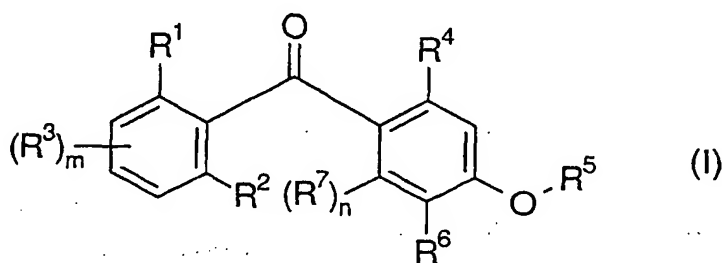
## Description

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The present invention relates to a fungicidal composition comprising a fungicidally acceptable carrier and/or surface active agent and synergistically effective amounts of

10 (a) at least one benzophenone of formula I

15



20

wherein

R<sup>1</sup> represents a halogen atom, an optionally substituted alkyl, alkanoyloxy, alkoxy group or a hydroxy group;

25

R<sup>2</sup> represents a halogen atom or an optionally substituted alkyl group,

m is 0 or an integer of 1 to 3;

30

R<sup>3</sup> independently represents a halogen atom, an optionally substituted alkyl or alkoxy group or a nitro group;

R<sup>4</sup> represents a halogen atom, a cyano, carboxy, hydroxy or nitro group or an optionally substituted alkyl, alkoxy, alkenyl, alkylthio, alkylsulphanyl, alkylsulphonyl or amino group;

35

R<sup>5</sup> represents an optionally substituted alkyl group;

R<sup>6</sup> represents a halogen atom or a nitro group, an optionally substituted alkyl, alkoxy, alkenyloxy, alkynyloxy, alkylthio, cycloalkyl, cycloalkyloxy, aryloxy group;

40

n is 0 or 1; and

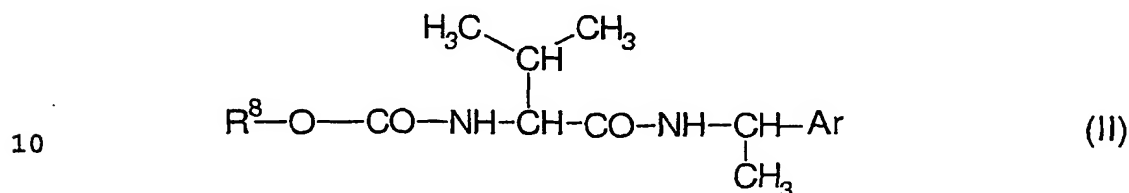
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R<sup>7</sup> independently represents a halogen atom, an optionally substituted alkyl, alkenyl, alkynyl, alkoxy, alkenyloxy, alkynyloxy, cycloalkyl, cycloalkoxy group; and

(b) at least one valinamid of formula II

5



in which

15

R<sup>8</sup> represents alkyl and

Ar represents Aryl or hetaryl, whereby

20 aryl represents a phenyl or naphthyl moiety

and

25 hetaryl represents a benzthiazolyl, benzimidazolyl or benzoxazolyl moiety,

where if desired, these aromatic radicals can carry one to three substituents selected from the group consisting of halogen, C<sub>1-6</sub> alkyl and C<sub>1-6</sub> alkoxy.

30

The fungicidal compounds of formula I to be used according to the present invention are known for example from US patent US 5,773,663. In addition, US 5,773,663 suggests to combine fungicidal benzophenone derivatives with other fungicides.

35

However, there is no hint that such mixtures show synergistic effects and can advantageously be used for controlling diseases such as grape downy mildew or others. The fungicidal compounds of formula II are known for example from EP 0 472996, DE-A 4321897, 40 WO-A 96 07638, DE 19531814 and JP-A 09 323984.

Although mixtures comprising either benzophenones of formula I (EP 1023834) or valinamides of formula II (WO 99 56551) as active ingredients are described, mixtures comprising both benzophenones 45 and valinamides have not been described yet.

Surprisingly, a strong synergy between the compounds of formula I and the compounds of formula II in greenhouse trials was found when these two compounds were in-tank mixed and when the activity of these mixtures was compared with that of the solo activity of 5 each active ingredient.

A mixture of fungicides shows synergistic effect if the fungicidal activity of the mixture is larger than the sum of activities of the separately applied compounds. The expected fungicidal 10 activity for a given mixture of two fungicides can also be calculated as follows (See Colby, S.R., "Calculating synergistic and antagonistic response of herbicide combinations", Weeds 15, pp 20-22 (1967)):

15

$$EE = x + y - x \cdot y / 100$$

wherein

20 x is the efficacy in % compared with an untreated control upon treatment with a fungicidal active ingredient A at a dose rate a;

25 y is the efficacy in % compared with an untreated control upon treatment with a fungicidal active ingredient B at a dose rate b;

EE is the expected efficacy with a combination of fungicidal active ingredients A and B at a dose of a + b, respectively. 30

If the actual efficacy (E) exceeds the expected (calculated) one (EE), the mixture displays a synergistic effect.

35 The present invention includes a fungicidal composition comprising an acceptable carrier and/or surface active agent and synergistically effective amounts of at least one compound of formula I, and at least one compound of formula II.

40 The present invention also includes a method of controlling the growth of phytopathogenic fungi at a locus which comprises applying synergistically effective amounts of at least one benzo-phenone of formula I and at least one compound of formula II as defined above to the locus.

45 All moieties mentioned for the substituents R<sub>1</sub> to R<sub>7</sub> of formula I as well as R<sub>8</sub> and the substituents of the Ar-moiety of formula II, R<sub>9</sub> and R<sub>10</sub> are collective terms for individual enumerations of

the individual members of a group. For all alkyl moieties and the alkyl moieties of alkoxy, alkanoyloxy, alkylthio, alkylsulfonyl and alkylsulfinyl a C<sub>1-6</sub> alkyl moiety is preferred. For all alkenyl moieties or the alkenyl moieties of alkenyloxy a C<sub>2-6</sub> alkenyl moiety is preferred. For all alkynyl moieties or the alkynyl moieties of alkynyloxy a C<sub>2-6</sub> alkynyl moiety is preferred. For all cycloalkyl moieties or the cycloalkyl moieties of cycloalkyloxy a C<sub>3-8</sub> alkyl moiety is preferred.

10 For example

- halogen is fluorine, chlorine, bromine and iodine;
- alkyl is straight-chain or branched alkyl groups having 1 to 6 carbonatoms such as methyl, ethyl, propyl, 1-methyl-ethyl, butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethyl-ethyl, pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, hexyl, 1,1-dimethyl-propyl, 1,2-dimethylpropyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,2-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 1-ethylbutyl, 2-ethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl, 1-ethyl-1-methylpropyl and 1-ethyl-2-methylpropyl;
- C<sub>3-6</sub> cycloalkyl or the cycloalkyl moiety of cycloalkoxy is a monocyclic alkyl group having 3 to 6 carbon ring members, eg. cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl;
- C<sub>2-6</sub> alkenyl is a straight-chain or branched alkenyl group having 2 to 6 carbon atoms and a double bond in any desired position, such as ethenyl, 1-propenyl, 2-propenyl, 1-methylethenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1-methyl-1-propenyl, 2-methyl-1-propenyl, 1-methyl-2-propenyl, 2-methyl-2-propenyl, 1-pentenyl, 2-pentenyl, 3-pentenyl, 4-pentenyl, 1-methyl-1-butenyl, 2-methyl-1-butenyl, 3-methyl-1-butenyl, 1-methyl-2-butenyl, 2-methyl-2-butenyl, 3-methyl-2-butenyl, 1-methyl-3-butenyl, 2-methyl-3-butenyl, 3-methyl-3-butenyl, 1,1-dimethyl-2-propenyl, 1,2-dimethyl-1-propenyl, 1,2-dimethyl-2-propenyl, 1-ethyl-1-propenyl, 1-ethyl-2-propenyl, 1-hexenyl, 2-hexenyl, 3-hexenyl, 4-hexenyl, 5-hexenyl, 1-methyl-1-pentenyl, 2-methyl-1-pentenyl, 3-methyl-1-pentenyl, 4-methyl-1-pentenyl, 1-methyl-2-pentenyl, 2-methyl-2-pentenyl, 3-methyl-2-pentenyl, 4-methyl-2-pentenyl, 1-methyl-3-pentenyl, 2-methyl-3-pentenyl,

## 5

3-methyl-3-pentenyl, 4-methyl-3-pentenyl,  
1-methyl-4-pentenyl, 2-methyl-4-pentenyl,  
3-methyl-4-pentenyl, 4-methyl-4-pentenyl,  
1,1-dimethyl-2-butenyl, 1,1-dimethyl-3-butenyl,  
5 1,2-dimethyl-1-butenyl, 1,2-dimethyl-2-butenyl,  
1,2-dimethyl-3-butenyl, 1,3-dimethyl-1-butenyl,  
1,3-dimethyl-2-butenyl, 1,3-dimethyl-3-butenyl,  
2,2-dimethyl-3-butenyl, 2,3-dimethyl-1-butenyl,  
2,3-dimethyl-2-butenyl, 2,3-dimethyl-3-butenyl,  
10 3,3-dimethyl-1-butenyl, 3,3-dimethyl-2-butenyl,  
1-ethyl-1-butenyl, 1-ethyl-2-butenyl, 1-ethyl-3-butenyl,  
2-ethyl-1-butenyl, 2-ethyl-2-butenyl, 2-ethyl-3-butenyl,  
1,1,2-trimethyl-2-propenyl, 1-ethyl-1-methyl-2-propenyl,  
1-ethyl-2-methyl-1-propenyl and  
15 1-ethyl-2-methyl-2-propenyl;

C<sub>2-6</sub> alkynyl is a straight-chain or branched alkynyl groups  
having 2 to 6 carbon atoms and a triple bond in any desired  
position, such as ethynyl, 2-propynyl, 2-butyne,  
20 3-butyne, 1-methyl-2-propynyl, 2-pentyne, 3-pentyne,  
4-pentyne, 1-methyl-2-butyne, 1-methyl-3-butyne,  
2-methyl-3-butyne, 1,1-dimethyl-2-propynyl,  
1-ethyl-2-propynyl, 2-hexynyl, 3-hexynyl, 4-hexynyl,  
5-hexynyl, 1-methyl-2-pentyne, 1-methyl-3-pentyne,  
25 1-methyl-4-pentyne, 2-methyl-3-pentyne, 2-methyl-  
4-pentyne, 3-methyl-4-pentyne, 4-methyl-2-pentyne,  
1,1-dimethyl-2-butyne, 1,1-dimethyl-3-butyne,  
1,2-dimethyl-3-butyne, 2,2-dimethyl-3-butyne,  
1-ethyl-2-butyne, 1-ethyl-3-butyne, 2-ethyl-3-butyne and  
30 1-ethyl-1-methyl-2-propynyl;

aryl or aryloxy, is a aromatic mono- or polycyclic hydrocarbon  
radical which are bonded to the structure directly or (aryloxy)  
via an oxygen atom (-O-) eg. phenyl and naphthyl or phenoxy and  
35 naphthyloxy;

Hetaryl is a benzo-fused 5-membered heteroaryl, containing  
one to two nitrogen atom and/or an oxygen or sulfur atom,  
e.g. bezhiazolyl, benzimidazolyl or bezoxazolyl;

40 Halophenyl is a phenyl moiety, substituted with 1 to 5  
halogen atoms in position 2,3,4,5 and/or 6;

45 Fluorophenyl is a phenyl moiety, substituted with 1 to 5  
fluorine atoms in position 2,3,4,5 and/or 6;

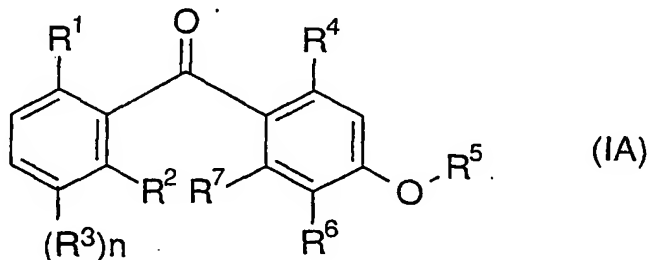
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- Alkylphenyl is a phenyl moiety, substituted with 1 to 5 C<sub>1-6</sub> alkyl moieties in position 2,3,4,5, and/or 6;
- Methylphenyl is a phenyl moiety substituted with 1-5 methyl moieties in position 2,3,4,5 and/or 6;

Preferred compounds of formula I are benzophenones of formula IA,

10

15



wherein

- 20 R<sup>1</sup> represents a halogen atom, a methyl, trifluoromethyl or a C<sub>1-4</sub>-alkoxy group or a hydroxy group in particular a chloro atom, a methyl, an acetoxy, a methoxy or a hydroxy group;
- 25 R<sup>2</sup> represents a halogen atom, in particular a chloro atom or a methyl group;
- R<sup>3</sup> represents a bromo or chloro atom, a methyl, trifluoromethyl or nitro group, in particular a bromine or chlorine atom or a methyl group;
- 30 R<sup>4</sup> represents a methyl group;
- R<sup>5</sup> represents an alkyl group, most preferred a C<sub>1-4</sub>-alkyl group, in particular a methyl group;
- 35 R<sup>6</sup> and R<sup>7</sup> each independently represent an alkoxy group which may be substituted by a phenyl, alkylphenyl or halophenyl group, preferably C<sub>1-6</sub>-alkoxy being optionally substituted by a phenyl, methylphenyl or fluorophenyl group, in particular methoxy, benzyl-oxy and 2-fluorobenzyloxy; and
- 40

n is 0 or 1.

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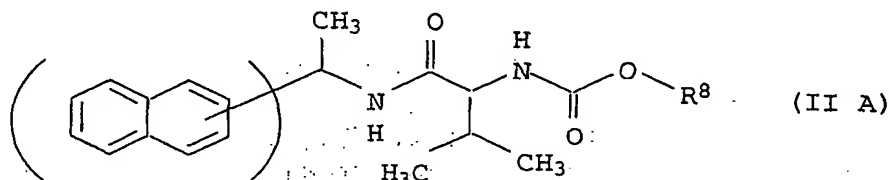
Particularly preferred are the benzophenones selected from the group consisting of 6'-butoxy-2,6-dichloro-4',5'-dimethoxy-2'-methylbenzophenone coded BP-1, 2,6-dichloro-4',5'-dimethoxy-6'-(2-fluorobenzyloxy)-2'-methylbenzophenone coded BP-2, 6'-benzyloxy-4',5'-dimethoxy-2,6-dimethyl-2'-methylbenzophenone coded BP-3, 5-bromo-2',6-dimethyl-2,4',5',6'-tetramethoxybenzophenone coded BP-4 and 2,6-dichloro-2'-methyl-4',5',6'-trimethoxybenzophenone coded BP-5, most preferred is BP-4.

10 In valinamides of formula II  $R^8$  represents a  $C_{1-6}$  alkyl-group, particularly preferred a branched  $C_{3-6}$  alkyl group most preferred an isopropyl or *sec*-butyl group.

Preferred compounds of formula II are valinamides of formula IIA

15

20



wherein

25

Ar represents naphthyl, most preferred bonded to the structure via position 2

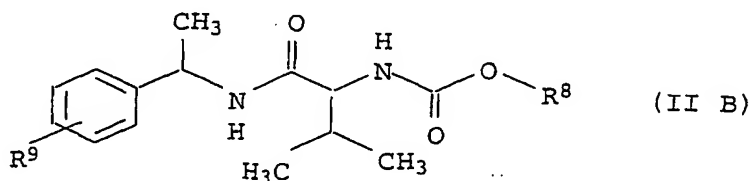
wherein most preferred is compound VA1

30 ([2-methyl-1-[1-(naphth-2-yl)-ethylaminocarbonyl]-propyl]-carbamate isopropyl ester);

of formula II B

35

40



wherein

45 Ar represents phenyl and



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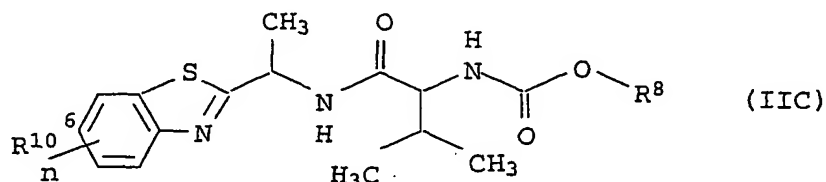
R<sup>9</sup> represents halogen, most preferred chlorine, a straight, chained C<sub>1-6</sub> alkyl or C<sub>1-6</sub> alkocy group, in particular a methyl, ethyl or methoxy group, most preferred bonded to the structure via position 4,

5

wherein most preferred is iprovalicarb ([2-methyl-1-[1-(4-methyl-phenyl)-ethylaminocarbonyl]-propyl]-carbamic acid isopropyl ester);

10 and of formula II C

15



20 wherein

Ar represents benzthiazol-2-yl,

R<sup>10</sup> represents a halogen atom particularly a fluorine atom most preferred bonded to the structure in position 6 and

25

n has a value of 0 or 1, 2 or 3, most preferred 1,

wherein most preferred is VA2, ([2-methyl-1-[1-(6-fluorobenzthiazol-2-yl)-ethylaminocarbonyl]-propyl]-carbamic acid isopropyl ester);

30

Preferred are co-formulations, comprising the following constituents:

35

- a carrier;
- at least one benzophenone of formula I,
- at least one compound of formula II
- optionally an adjuvant selected from the group consisting of polyalkoxylated alcohols, triglycerides and amines, in particular Synperonic<sup>®</sup> 91-6, which is commercially available from Uniqema, formerly ICI Surfactants;

45

- optionally a foam breaking agent.

The compound of formula I and the compound of formula II are to be applied together, in synergistically effective amounts. These synergistic mixtures exhibit an extraordinary efficacy against a broad range of phytopathogenic fungi, in particular against fungi from the classes ascomycetes, basidiomycetes, oomycetes and deuteromycetes. Therefore, they can be applied advantageously against a broad range of diseases in different crops. They may be applied as leaf, stem, root, into-water, seed dressing, nursery box or soil fungicides.

The mixture according to the invention may be preferably applied for controlling phytopathogenic fungi of the genera:

- 15 Achlya, Alternaria, Balansia, Bipolaris, Blumeria, Botrytis, Cercospora, Cochliobolus, Curvularia, Cylindrocladium, Drechslera, Entyloma, Erysiphe, Fusarium, Gaeumannomyces, Gerlachia, Gibberella, Guignardia, Leptosphaeria, Magnaporthe, Monilinia, 20 Mucor, Mycosphaerella, Myrothecium, Nigrospora, Peronospora, Phoma, Phytophthora, Podosphaera, Plasmopara, Pseudoperonospora, Pseudocercospora, Puccinia, Pyrenophora, Pyricularia, Pythium, Rhizoctonia, Rhizopus, Rhynchosporium, Sarocladium, Sclerophthora, Sclerotinia, Sclerotium, Septoria, Tilletia, Uncinula, 25 Ustilago, Ustilaginoidea, and Venturia, in particular the species Plasmopara viticola, Phytophthora sp., Pseudoperonospora sp., and Bremia sp.

The mixtures according to the invention are in particular applied for controlling the above phytopathogenic fungi on dicotyledoneous plants, such as grapes, tobacco, potato, tomato, fruit crops, oil seed crops, vegetables and ornamentals, and monocotyledoneous crops.

- 35 The application rate of the compound of formula I according to this invention is usually in the range of 1 to 2000 grams of active ingredient (g a.i.) per hectare, with rates between 20-500 g a.i./ha often achieving satisfactory control. The optimal rate for a specific application will depend on the crop(s) 40 under cultivation and the predominant species of infesting fungi, and readily may be determined by established biological tests known to those skilled in the art.

In general, the preferred application rate of the compounds of formula I is in the range of 10 to 500 g a.i./ha, preferably 20-400 g a.i./ha.

The optimal rate for the compound of formula II will, however, depend on the crop(s) under cultivation and the level of infestation by the fungus, and can readily be determined by established biological tests.

5

The ratio (by weight) of the compound of formula I to the compound of formula II is as a rule, from 100 : 1 to 1 : 100. The preferred ratio formula I : formula II may vary, e.g., from about 10 : 1 to about 1 : 10, in particular from about 5 : 1 to  
10 about 1 : 5, most preferred from 3 : 1 to 1 : 3.

The active compounds can be co-formulated together in a suitable ratio according to the present invention, together with usual carriers or diluents and/or additives known in the art.

15

Accordingly the invention further provides a fungicidal composition which comprises a carrier and, as active ingredient, at least one compound of formula I as defined above and at least one compound of formula II as defined above.

20

A method of making such a composition is also provided which comprises bringing the compound of formula I and the compound of formula II into association with at least one carrier. It is also envisaged that different isomers or mixtures of isomers of formula I and/or the compound of formula II may have different levels or spectra of activity and thus compositions may comprise individual isomers or mixtures of isomers.

A composition according to the invention preferably contains from  
30 0.1% to 99.9%, preferably 0.2 to 80 % by weight (w/w) of active ingredients.

A carrier in a composition according to the invention is any material with which the active ingredient is formulated to facilitate application to the locus to be treated, which may for  
35 example be a plant, seed, foliage, soil, or into the water where the plant grow, or to the roots or to facilitate storage, transport or handling. A carrier may be a solid or a liquid, including material which is normally a gas but which has been  
40 pressed to form a liquid.

The compositions may be manufactured into e.g. emulsion concentrates, solutions, oil in water emulsions, wettable powders, soluble powders, suspension concentrates, dusts, granules, water  
45 dispersible granules, tablets, micro-capsules, gels and other formulation types by well-established procedures. These procedures include intensive mixing and/or milling of the active in-

gredients with other substances, such as fillers, solvents, solid carriers, surface active compounds (surfactants), and optionally solid and/or liquid auxiliaries and/or adjuvants. The form of application such as spraying, atomizing, dispersing or pouring  
5 may be chosen like the compositions according to the desired objectives and the given circumstances.

Solvents may be aromatic hydrocarbons, e.g. Solvesso<sup>®</sup> 200, substituted naphthalenes, phthalic acid esters, such as dibutyl or  
10 dioctyl phthalate, aliphatic hydrocarbons, e.g. cyclohexane or paraffins, alcohols and glycols as well as their ethers and esters, e.g. ethanol, ethyleneglycol mono- and dimethyl ether, ketones such as cyclohexanone, strongly polar solvents such as N-methyl-2-pyrrolidone, or  $\gamma$ -butyrolactone, higher N-alkylpyrrolidones, e.g. N-octylpyrrolidone or N-cyclohexylpyrrolidone, epoxi-  
15 dized plant oil esters, e.g. methylated coconut or soybean oil ester and water. Mixtures of different liquids are often suitable.

20 Solid carriers, which may be used for dusts, wettable powders, water dispersible granules, or granules, may be mineral fillers, such as calcite, talc, kaolin, montmorillonite or attapulgite or others. The physical properties may be improved by addition of highly dispersed silica gel or polymers. Carriers for granules  
25 may be porous material, e.g. pumice, kaolin, sepiolite, bentonite; non-sorptive carriers may be calcite or sand or others. Additionally, a multitude of pre-granulated inorganic or organic materials may be used, such as dolomite or crushed plant residues.

30 Pesticidal compositions are often formulated and transported in a concentrated form which is subsequently diluted by the user before application. The presence of small amounts of a carrier which is a surfactant facilitates this process of dilution. Thus,  
35 preferably at least one carrier in a composition according to the invention is a surfactant. For example, the composition may contain at two or more carriers, at least one of which is a surfactant.

40 Surfactants may be nonionic, anionic, cationic or zwitterionic substances with good dispersing, emulsifying and wetting properties depending on the nature of the compound according to general formula I to be formulated. Surfactants may also mean mixtures of individual surfactants.  
45

The compositions of the invention may for example be formulated as wettable powders, water dispersible granules, dusts, granules, solutions, emulsifiable concentrates, emulsions, suspension concentrates and aerosols. Wettable powders usually contain 5 to 90% w/w of active ingredient and usually contain in addition to solid inert carrier, 3 to 10% w/w of dispersing and wetting agents and, where necessary, 0 to 10% w/w of stabilizer(s) and/or other additives such as penetrants or stickers. Dusts are usually formulated as a dust concentrate having a similar composition to that of a wettable powder but without a dispersant, and may be diluted in the field with further solid carrier to give a composition usually containing 0.5 to 10% w/w of active ingredient. Water dispersible granules and granules are usually prepared to have a size between 0.15 mm and 2.0 mm and may be manufactured by a variety of techniques. Generally, these types of granules will contain 0.5 to 90% w/w active ingredient and 0 to 20% w/w of additives such as stabilizer, surfactants, slow release modifiers and binding agents. The so-called "dry flowables" consist of relatively small granules having a relatively high concentration of active ingredient. Emulsifiable concentrates usually contain, in addition to a solvent or a mixture of solvents, 1 to 80% w/v active ingredient, 2 to 20% w/v emulsifiers and 0 to 20% w/v of other additives such as stabilizers, penetrants and corrosion inhibitors. Suspension concentrates are usually milled so as to obtain a stable, non-sedimenting flowable product and usually contain 5 to 75% w/v active ingredient, 0.5 to 15% w/v of dispersing agents, 0.1 to 10% w/v of suspending agents such as protective colloids and thixotropic agents, 0 to 10% w/v of other additives such as defoamers, corrosion inhibitors, stabilizers, penetrants and stickers, and water or an organic liquid in which the active ingredient is substantially insoluble; certain organic solids or inorganic salts may be present dissolved in the formulation to assist in preventing sedimentation and crystallization or as antifreeze agents for water.

Aqueous dispersions and emulsions, for example compositions obtained by diluting the formulated product according to the invention with water, also lie within the scope of the invention.

Of particular interest in enhancing the duration of the protective activity of the compounds of this invention is the use of a carrier which will provide slow release of the pesticidal compounds into the environment of a plant which is to be protected.

The biological activity of the active ingredient can also be increased by including an adjuvant in the formulation or the spray dilution. An adjuvant is defined here as a substance which can increase the biological activity of an active ingredient but is not itself significantly biologically active. The adjuvant can either be included in the formulation as a coformulant or carrier, or can be added to the spray tank together with the formulation containing the active ingredient.

10 As a commodity the compositions may preferably be in a concentrated form whereas the end user generally employs diluted compositions. The compositions may be diluted to a concentration down to 0.001% of active ingredient. The doses usually are in the range from 0.01 to 10 kg a.i./ha.

15 Examples of formulations which can be used according to the invention are:

SC-I 1

20

Active ingredient	BP-1	100.0 g
Dispersing agent	Morwet D425 1)	25.0 g
Dispersing agent	Pluronic® PE105002)	5.0 g
25 Antifoaming agent	Rhodorsil® 426R 3)	1.5 g
Dispersing agent	Rhodopol® 23 4)	2.0 g
Antifreezing agent	Propylene glycol	80.0 g
Biocidal agent	Proxel® GXL 5)	1.0 g
Water		to 1000 ml

30

SC-I 2

Active ingredient	BP-4	100.0 g
Dispersing agent	Soprophor® FL 6)	30.0 g
Antifoaming agent	Rhodorsil® 426R 3)	1.5 g
35 Dispersing agent	Rhodopol® 23 4)	2.0 g
Antifreezing agent	Propylene glycol	80.0 g
Biocidal agent	Proxel® GXL 5)	1.0 g
Water		to 1000 ml

40 SC-IP

Active ingredient	iprovalicarb	200.0 g
Dispersing agent	Soprophor® FL 6)	25.0 g
Antifoaming agent	Rhodorsil® 426R 3)	1.5 g
45 Dispersing agent	Rhodopol® 23 4)	2.0 g
Antifreezing agent	Propylene glycol	80.0 g

14

	Biocidal agent	Proxel <sup>®</sup> GXL 5)	1.0 g
	Water		to 1000 ml
	<u>SC-I + IP</u>		
5	Active ingredient	BP-4	60.0 g
	Active ingredient	iprovalicarb	120.0 g
	Dispersing agent	Soprophor <sup>®</sup> FL 6)	25.0 g
	Antifoaming agent	Rhodorsil <sup>®</sup> 426R 3)	1.5 g
	Dispersing agent	Rhodopol <sup>®</sup> 23 4)	2.0 g
10	Antifreezing agent	Propylene glycol	80.0 g
	Biocidal agent	Proxel <sup>®</sup> GXL 5)	1.0 g
	Water		to 1000 ml
	<u>DC-I 1</u>		
15	Active ingredient	BP-4	100.0 g
	Wetting agent	Pluronic <sup>®</sup> PE6400 7)	50.0 g
	Dispersing agent	Lutensol <sup>®</sup> TO 12 8)	50.0 g
	Solvent	benzyl alcohol	to 1000 ml
20	1) Morwet <sup>®</sup> D425	(Na-salt of a naphthalene-formaldehyde-condensate; Witco)	
	2) Pluronic <sup>®</sup> PE10500	(Polyethyleneoxid/Polypropyleneoxid block copolymer; BASF)	
25			
	3) Rhodorsil <sup>®</sup> 426R	(silicone oil; Rhône-Poulenc)	
	4) Rhodopol <sup>®</sup> 23	(Polysaccharide based dispersing agent; Rhône-Poulenc)	
30			
	5) Proxel <sup>®</sup> GXL	(20% aqueous dipropylene glycol solution of 1,2-Benzisothiazolin-3-one; Zeneca)	
	6) Soprophor <sup>®</sup> FL	(Triethanolamoniums salt of oxethylated poly-arylphenolphosphate; Rhône-Poulenc)	
35			
	7) Pluronic <sup>®</sup> PE6400	(Polyethyleneoxid/Polypropyleneoxid block-copolymer; BASF)	
40			
	8) Lutensol <sup>®</sup> TO12	(alkoxylated oxo-fatty acids; BASF)	

45 The formulation SC-IP comprising a compound of formula II is in-tank mixed with any of the other formulations SC-I 1, SC-I 2, SC-I 3, or DC-I which comprise the compound of formula I.

15

In a preferred embodiment the active ingredients are added to the tank mix together each as solo formulation.

Therefore, the present invention relates to a kit for the preparation of a spray mixture consisting of two separate containments:

(i) a containment which comprises at least one benzophenone of formula I, in particular one or more compounds selected from BP-1 through BP-4, conventional carriers and optionally adjuvants;

(ii) a containment which comprises at least one compound of formula II.

15

In a preferred embodiment the said kit will consist of two bottles with dispensing means which allow the easy and correct addition of the active ingredients (a) and (b) to the tank mix.

The formulation SC-I + IP comprising BP-4 and iprovalicarb can be used directly for preparing the tank mix according to the present invention.

A composition according to the invention preferably contains from 0.5% to 95% by weight of active ingredients.

As commodity the compositions may preferably be in a concentrated form whereas the end-user generally employs diluted compositions. The compositions may be diluted down to a concentration of 0.0001% of active ingredients.

The compositions of this invention can be applied to the plants or their environment simultaneous with or in succession with other active substances. These other active substances can be either fertilizers, agents which donate trace elements or other preparations which influence plant growth. However, they can also be other fungicides, selective herbicides, insecticides, bactericides, nematocides, algicides, molluscicides, rodenticides, virucides, compounds inducing resistance into plants, biological control agents such as viruses, bacteria, nematodes, fungi and other microorganisms, repellents of birds and animals, and plant growth regulators, or mixtures of several of these preparations, if appropriate together with other carrier substances conventionally used in the art of formulation, surfactants or other additives which promote application.



## 16

Examples of insecticidal compounds are alpha-cypermethrin, benflu-racarb, fenobucarb (BPMC), buprofezine, carbosulfan, cartap, chlorfenvinphos, chlorpyrifos-methyl, cycloprothrin, cyperme-thrin, esfenvalerate, ethofenprox, fenpropathrin, flucythrinate, 5 flufenoxuron, hydramethylnon, imidacloprid, isoxathion, fenitro-thion (MEP), fenthion (MPP), nitenpyram, phenthoate (PAP), perme-thrin, propaphos, pymetrozine, silafluofen, tebufenozide, teflu-benzuron, temephos, terbufos, tetrachlorvinphos and triazamate.

10 Examples of biological control agents are: *Bacillus thuringien-sis*, *Verticillium lecanii*, *Autographica californica* NPV, *Beauva-ria bassiana*, *Ampelomyces quisqualis*, *Bacilis subtilis*, *Pseudo-monas cholororaphis*, *Pseudomonas fluorescens*, *Steptomyces griseo-viridis* and *Trichoderma harzianum*.

15

Examples of chemical agents that induce systemic acquired resis-tance in plants such are: isonicotinic acid or derivatives thereof, 2,2-dichloro-3,3-dimethylcyclopropylcarboxylic acid.

20 The present invention is of wide applicability in the protection of crops, trees, residential and ornamental plants against fungal attack. Preferred crops are cereals, such as wheat and barley, rice as well as vines and apples. The duration of the protection is normally dependent on the individual compound selected, and 25 also a variety of external factors, such as climate, whose impact is normally mitigated by the use of a suitable formulation. The following examples further illustrate the present invention. It should be understood, however, that the invention is not lim-ited solely to the particular examples given below.

30

## EXAMPLES

## General Methods

35 The trials are carried out under greenhouse conditions in resid-ual or curative applications. The fungicides are applied in single treatments, or in a combination comprising a benzophenone of formula I and a compound of formula II. The compounds are applied in form of an aqueous spray mix obtained from concen- 40 trated formulation or the technical material.

Grape plants of variety "Mueller-Thurgau" are grown in the green-house from small stake cuttings. When about 40 cm high, the num-ber of leaves is reduced to 4 fully expanded leaves per plant.

45

The compounds are dissolved in acetone with 0.5% TRITON® X155 (an alkylaryl polyether alcohol), and sprayed in concentrations and combinations as given in tables I and II with a three nozzle overhead fungicide sprayer to near run-off. Plants are then allowed to air-dry.

Inoculation precedes treatment in the case of curative evaluations and follows treatment in case of residual evaluations.

10 For inoculation an aqueous spore suspension of the pathogen is applied to the plant and the plants are kept 1-2 days in a moist infection chamber before being returned to the greenhouse where they are maintained by bottom watering.

15 Disease on the foliage as percent leaf area with disease symptoms/signs is evaluated about 7 days after inoculation.

$$\% \text{ disease control} = 100 - \frac{\% \text{ disease in treated plants}}{\% \text{ disease in untreated plants}} \times 100\%$$

Two kinds of controls are included in the tests:

- Plants treated with the solvent/surfactant solution and inoculated (Solvent Blank).
- Untreated plants which are inoculated (Inoculated Control).

Evaluation of the disease:

Assessments of the diseases took place at the indicated day after the application of the compounds. Per cent infected leaf area infected was evaluated. The efficacy of the compounds/compounds mixtures to control the diseases was calculated by using the formula given above.

Determination of synergy:

Synergy was calculated using the % disease control values of specific treatments for the two COLBY formula given hereinabove

Example 1

Fungicidal efficacy of the mixture of BP-4 + iprovalicarb (2 day curative) against *Plasmopara viticola* on grapes

18

The tank mix was obtained from technical materials of BP-4 and iprovalicarb. The observed and expected efficacies with different rates are given in Table I:

5 Table I

dose rate (ppm)		Observed Efficacy	Expected Efficacy
			cacy
BP-4	iprovalicarb		
10 27	0	2	--
9	0	0	--
3	0	0	--
1	0	0	--
0.33	0	0	--
0.11	0	0	--
15 0.037	0	0	--
0	9	91	--
0	3	63	--
0	1	11	--
0	0.33	2	--
20 0	0.11	0	--
27	9	97	91
9	9	96	91
9	3	71	63
3	3	73	63
1	3	66	63
25 3	1	15	11
1	1	16	11
0.33	1	23	11
1	0.33	6	2
0.11	0.33	5	2
30 0.33	0.11	5	0
0.037	0.11	3	0

## Example 2

35 Fungicidal efficacy of the mixture of BP-4 + iprovalicarb (3 day residual) against *Plasmopara viticola* on grapes

The tank mix was obtained from technical materials of BP-4 and iprovalicarb. The observed and expected efficacies with different rates are given in Table II:

40

Table II

	dose rate (ppm)		Observed Efficacy	Expected Efficacy
		<u>iprovalicarb</u>		
5	<u>BP-4</u>			
	27	0	6	--
	9	0	4	--
	3	0	1	--
	1	0	0	--
	0.33	0	0	--
10	0.11	0	0	--
	0.037	0	0	--
	0	9	90	--
	0	3	55	--
	0	1	11	--
15	0	0.33	3	--
	0	0.11	0	--
	9	9	95	90
	9	3	68	57
	3	3	69	55
	1	3	63	55
20	3	1	26	12
	1	1	33	11
	0.33	1	20	11
	1	0.33	5	3
	0.11	0.33	8	3
25	0.33	0.11	5	0
	0.037	0.11	6	0

## Example 3

- 30 Fungicidal efficacy of the mixtures of BP4 + VA1 and BP4 + VA2 against *Phytophthora infestans* on tomatoes

Leaves of potted plants of the "Große Fleischtomate St. Pierre" variety were sprayed to runoff with an aqueous suspension prepared from a stock solution consisting of 10% active ingredient, 63% cyclohexanone and 27% emulsifier. On the following day the leaves were infected with a cold aqueous zoospore suspension of *Phytophthora infestans* at a density of  $0.25 \times 10^6$  spores/ml. The plants were then set up in a water vapor-saturated chamber at from 18 to 20°C. After 6 days the disease had spread to such a great extent on the untreated but infected control plants that the attack could be assessed visually in %.

The visually determined values for the percentage of the leaf area attacked were converted into degrees of action as a percentage of the untreated control. The degree of action in the untreated control was set at 0. The degree of action when 0% of the

leaf area was attacked by fungus was set at 100. The expected degrees of action of the active ingredient composition were determined in accordance with the Colby formula (Colby, S.

R., "Calculating synergistic and antagonistic responses of herbicide combinations", Weeds, 15 pp. 20-22, 1967) and compared with the degrees of action observed.

Table III

10

Active ingredient	a.i. concentration in the spray liquor in ppm	Degree of action in % of the untreated control
control (untreated)	(98% attack)	0
<u>BP 4</u>	5	0
15	1	0
	0.2	0
<u>VA 1</u>	1	85
	0.2	8
<u>VA 2</u>	0.2	8
compositions according to the invention	observed degree of ac- tion	calculated degree of action *)
<u>BP4+</u>		
<u>VA1</u>	100	85
5 + 1 ppm mixture 5:1		
<u>BP4+</u>		
25	39	8
<u>VA1</u>		
5 + 0.2 ppm mixture 25:1		
<u>BP4+</u>		
<u>VA1</u>	100	85
1 + 1 ppm mixture 1:1		
30		
<u>BP4+</u>		
<u>VA2</u>	49	8
5 + 0.2 ppm mixture 25:1		
<u>BP4+</u>		
<u>VA2</u>	29	8
0.2 + 0.2 ppm mixture 1:1		

35

\*) calculated according to the Colby formula

These results show that the degree of action observed was higher for all mixture ratios than the degree of action calculated according to the Colby formula.

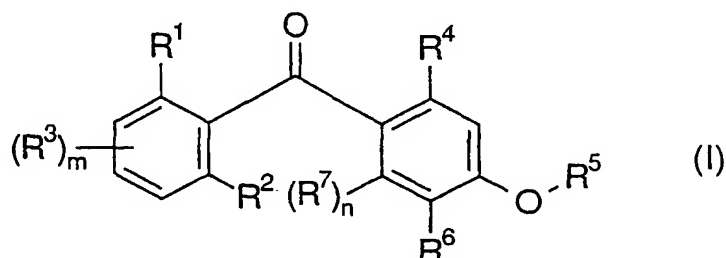
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What is claimed is:

1. A fungicidal composition comprising a fungicidally acceptable carrier and/or surface active agent and synergistically effective amounts of

(a) at least one benzophenone of formula I



wherein

R<sup>1</sup> represents a halogen atom, an optionally substituted alkyl, alkanoyloxy, alkoxy group or a hydroxy group,

R<sup>2</sup> represents a halogen atom or an optionally substituted alkyl group,

m is 0 or an integer of 1 to 3;

R<sup>3</sup> independently represents a halogen atom, an optionally substituted alkyl or alkoxy group or a nitro group;

R<sup>4</sup> represents a halogen atom, a cyano, carboxy, hydroxy or nitro group or an optionally substituted alkyl, alkoxy, alkenyl, alkylthio, alkylsulphinyl, alkylsulphonyl or amino group;

R<sup>5</sup> represents an optionally substituted alkyl group;

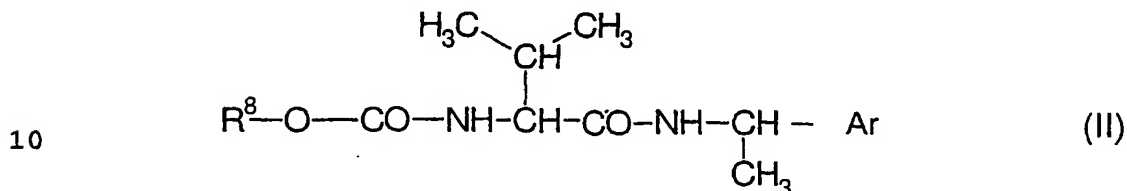
R<sup>6</sup> represents a halogen atom or a nitro group, an optionally substituted alkyl, alkoxy, alkenyloxy, alkynyloxy, alkylthio, cycloalkyl, cycloalkyloxy, aryloxy group;

n is 0 or 1; and

22

R<sup>7</sup> independently represents a halogen atom, an optionally substituted alkyl, alkenyl, alkynyl, alkoxy, alkenyloxy, alkynyloxy, cycloalkyl, cycloalkoxy group;

5 (b) at least one one valinamid of formula II



15 in which

R<sup>8</sup> represents C<sub>1</sub>-C<sub>6</sub> alkyl group;

Ar represents Aryl or hetaryl, whereby

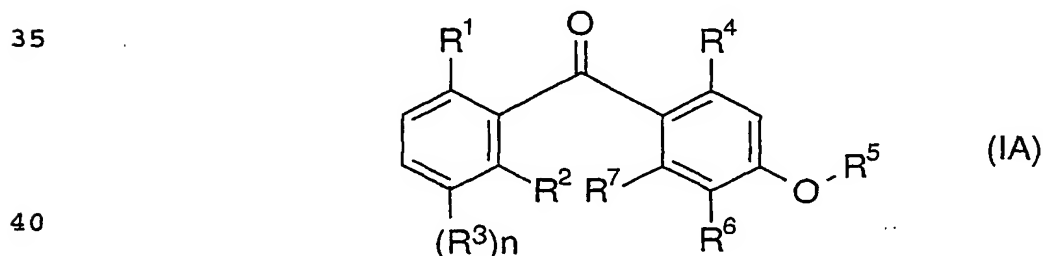
20 aryl represents a phenyl or naphtyl moiety,

and

25 hetaryl represents a benzthiazolyl, benzimidazolyl or benzoxazolyl moiety,

where, if desired, these aromatic radicals can carry one to three substituents selected from the group consisting of halogen, C<sub>1-6</sub> alkyl and C<sub>1-6</sub> alkoxy.

30 2. A composition as claimed in claim 1, wherein the benzophenone is a compound of formula IA,



wherein

45 R<sup>1</sup> represents a halogen atom, a methyl, trifluoromethyl, methoxy or hydroxy group, in particular a chlorine atom, a methyl or methoxy group;

23

R<sup>2</sup> represents a halogen atom, in particular a chloro atom or a methyl group;

5 R<sup>3</sup> represents a bromine or chlorine atom, a methyl, trifluoromethyl or nitro group, in particular a bromine atom;

R<sup>4</sup> represents a methyl group;

10 R<sup>5</sup> represents an alkyl group, in particular a methyl group;

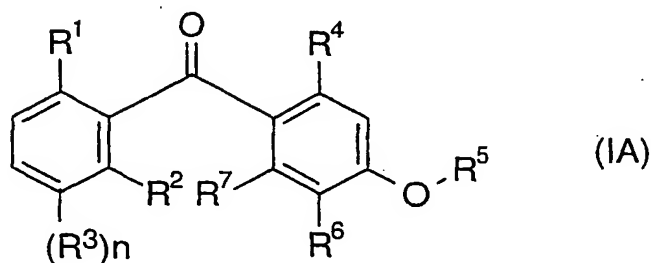
15 R<sup>6</sup> and R<sup>7</sup> each independently represent an alkoxy group which may be substituted by a phenyl, alkylphenyl or halophenyl group, preferably C<sub>1-6</sub>-alkoxy being optionally substituted by a phenyl, methylphenyl or fluorophenyl group, in particular methoxy, benzyl-oxy and 2-fluorobenzoyloxy; and

20 n is 0 or 1.

3. A composition as claimed in claim 1, wherein the benzophenone is a compound of formula IA,

25

30



wherein

35

R<sup>1</sup> represents a chloro atom, a methyl, acetoxy, methoxy or hydroxy group;

40

R<sup>2</sup> represents a chloro atom or a methyl group;

R<sup>3</sup> represents a bromo or chloro atom, or a methyl-group;

45

R<sup>4</sup> represents a methyl group;

R<sup>5</sup> represents an C<sub>1</sub>-C<sub>4</sub>-alkyl group;



R<sup>6</sup> and R<sup>7</sup> each independently represent a methoxy group and n is 0 or 1.

- 5 4. A composition as claimed in claim 1, wherein the benzophenone of formula I is selected from

6'-butoxy-2,6-dichloro-4',5'-dimethoxy-2'-methylbenzophenone;

- 10 2,6-dichloro-4',5'-dimethoxy-6'-(2-fluorobenzyloxy)-2'-methylbenzophenone;

6'-benzyloxy-4',5'-dimethoxy-2,6-dimethyl-2'-methylbenzophenone;

- 15 5-bromo-2',6-dimethyl-2,4',5',6'-tetramethoxybenzophenone; and

2,6-dichloro-2'-methyl-4',5',6'-trimethoxybenzophenone.

20

5. A composition as claimed in claim 1 comprising at least one compound of formula II, wherein R<sup>8</sup> represents a branched C<sub>3-6</sub> alkyl group, and Ar represents

- 25 a) a phenyl moiety carrying a C<sub>1-6</sub> alkyl moiety, a C<sub>1-6</sub> alkoxy moiety and/or halogen;  
b) a naphthyl moiety  
c) a benzthiazolyl, benzimidazolyl or benzoxazolyl moiety that can carry 0, 1, 2 or 3 halogen atoms.

30

6. A composition as claimed in claim 5, wherein R<sup>8</sup> represents an isopropyl or *sec*-butyl group, and Ar presents

- 35 a) a phenyl moiety carrying a chlorine, methyl, ethyl or methoxy group in position 4  
b) a naphth-2-yl moiety  
c) a benzthiazol-2-yl moiety that can carry 1 halogen atom in position 6.

- 40 7. A composition as claimed in claim 6, wherein the compound of formula II is [2-methyl-1-[1-(naphth-2-yl)-ethylamino-carbonyl]-propyl]-carbamic acid isopropyl ester, [2-methyl-1-[1-(6-fluorobenzthiazol-2-yl)-ethylamino-carbonyl]-propyl]-carbamic acid isopropyl ester or iprovali-carb ([2-methyl-1-[1-(4-methylphenyl)-ethylamino-carbonyl]-propyl]-carbamic acid isopropyl ester).
- 45

25

8. A composition as claimed in claim 1, wherein the ratio (by weight) of the benzophenone of formula I to the compound of formula II is from 10 : 1 to 1 : 10.

5 9. A composition as claimed in claim 8, wherein the ratio (by weight) of the benzophenone of formula I to the compound of formula II is from 5 : 1 to 1 : 5.

10 10. Method of controlling the growth of fungi at a locus which comprises applying a composition as claimed in claim 1 to the locus.

15 11. Method of controlling the growth of downy mildew at a locus which comprises applying a composition as claimed in claim 1 to the locus.

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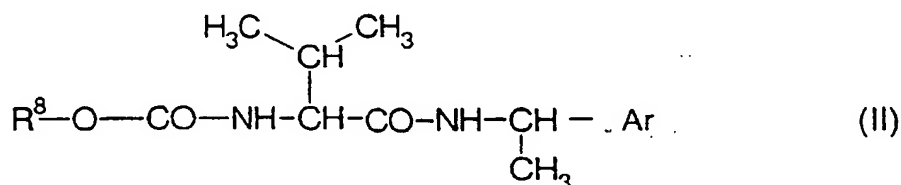
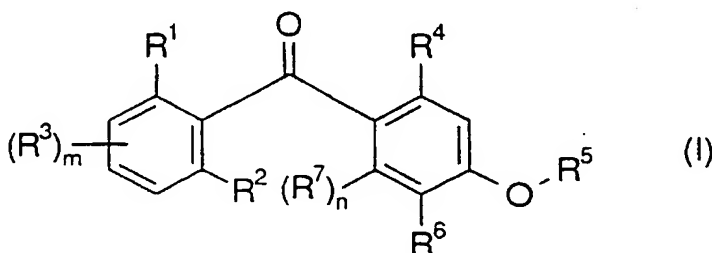
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(54) Title: FUNGICIDAL MIXTURES



(57) Abstract: The invention relates to a novel fungicidal composition comprising a fungicidally acceptable carrier and/or surface active agent and synergistically effective amounts of (a) at least one benzophenone of formula (I) wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, m and n have the meaning given; at least one compound of formula (II) in which Ar and R<sup>8</sup> have the meaning given; and to a method of controlling the growth of phytopathogenic fungi at a locus which comprises applying synergistically effective amounts of (a) at least one benzophenone of formula (I) and (b) at least one compound of formula (II) to the locus.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 01/01719

## A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO 00 76317 A (NOVARTIS ERFINDE VERWALT GMBH ;NOVARTIS AG (CH); DALTON IAN PAUL (C) 21 December 2000 (2000-12-21) claims -----	1-11

☐ Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 0076317	A	21-12-2000	AU 6427800 A	02-01-2001
			WO 0076317 A1	21-12-2000
			EP 1185173 A1	13-03-2002